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Prediction of volumetric properties of some fatty acid methyl esters, biodiesel fuels and their blends using perturbed Yukawa hard-core chain equation of state

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ABSTRACT

In this paper, a perturbed Yukawa hard-core chain (PYHCC) equation of state (EOS) has been employed for predicting the volumetric properties of some fatty acid methyl esters (FAMEs) and methyl ester-based biodiesel fuels and their blends. Three pure-component parameters appear in the PYHCC EOS, which reflect the chain-length, dispersive energy parameter and hard-core diameter of Yukawa fluid. These parameters have been determined by fitting of 56 experimental density data at ambient pressure. The performance of the proposed model has been assessed by predicting 1165 density data over pressure range from 0.1 to 130 MPa and temperature range from 278.4 to 396 K, for which their measured values were available in the literature. The overall average absolute deviation (AAD) of the correlated and predicted densities of studied FAMEs and biodiesels from literature data were found to be 0.26% and 0.52%, respectively. The isothermal compressibility (κ_T) coefficients have also been estimated by the use of proposed perturbed hard-chain equation of state (PHC EOS) and the results have been compared with those obtained from Tait equation; from 596 data points examined, AAD was found to be 2.60%. Besides, we have extended the mixture version of the proposed PHC EOS to binary and ternary blends formed by methyl ester-based biodiesels for predicting their volumetric properties. Our prediction accuracy has been checked by taking 406 experimental data points for above-mentioned blends, AAD was found to be 0.43%.

1. Introduction

Generally, biofuels came into focus recently as alternative energy sources by considering the depletion of oil resources as well as negative environmental impact associated with the use of fossil fuels [1].

In this regard, some chemistry and chemical engineering research interests have been specialized in this topic through the literature. Biodiesels are one of the plant-based biofuels, being promising future energy sources. The most common biodiesel production processes use methanol, which results in a product, comprised of a mixture of fatty acid methyl esters (FAMEs) [2–4]. Rapeseed, soybean, and palm oils are the most commonly used oils to produce biodiesel [5].

The properties of biodiesel are close to those of diesel fuels. The biodiesel was characterized by determining its viscosity, density, cetane number, cloud and pour points, characteristics of distillation, flash and combustion points and higher heating value (HHV) according to ISO norms. Density is one of the most important biodiesel properties, because engine injection systems (pumps and injectors) must deliver an amount of fuel precisely adjusted to provide a proper combustion while minimizing greenhouse gas emissions [6,7]. Besides, accurate knowledge of the thermophysical properties of biodiesels is valuable to model and optimize the combustion process involving biodiesel fuels.

Although some experimental data for thermophysical properties of FAMEs and methyl ester-based biodiesel fuels exist, prediction of these properties is an important issue with relevancy in many applications where FAMEs are considered as fluid design. On the other hand, the methyl ester-based biodiesels are promising options for the combustion process due to their non-toxicity and biodegradability. Under this circumstance, the development of

Abbreviations: FAME, fatty acid methyl ester; S, soybean; R, rapeseed; P, palm; SR, soybean + rapeseed; RP, rapeseed + palm; SP, soybean + palm; SRP, soybean + rapeseed + palm.

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Nomenclature and units

List of symbols

a_i	Values of coefficients in Eq. (9) for the case of λ = 1.8
AAD	average absolute deviation (%)
k_B	Boltzmann's constant (J K^{-1})
NP	number of data points
P	pressure (Pa)
T	Absolute temperature (K)
M_w	Molecular weight (g mol^{-1})
m	Chain length
R	Universal gas constant (J mol^{-1} K^{-1})
B_T	reduced bulk modulus
C, A_0, A_1, B_0, B_1 and B_2	coefficients that used in Eqs. (10)–(12)

Greek letters

$g(\sigma^+)$	pair radial distribution function of hard-cores at contact.
κ_T	isothermal compressibility coefficient.
η	hard-core chain packing fraction.
ρ	molar density (mol m^{-3}).
σ	hard-core diameter (nm).
ε	dispersive energy parameter (J).
λ	range parameter of attractive forces.

Superscripts

YHCC	Yukawa hard-core chain reference system.
pert.	perturbed system.
Lit.	literature data.
Calc.	calculated value.
Corr.	correlated value.
Exp.	experimental value.
Tait.	refers to the obtained values from the Tait equation.

equation of state (EOS) methods for predicting their thermophysical properties such as density and isothermal compressibility can be considerably useful.

A literature survey for the previous efforts on the modeling the thermophysical properties of biofuels are exemplified below.

Najafabadi et al. [8] have employed some local composition based models such as the Wilson, the non-random two-liquid (NRTL), and the Wilson-NRF to correlate and estimate the density, viscosity, and surface tension of biodiesels. Pratas et al. [9] have utilized an extended GCVOL group contribution method together with the Kay's mixing rules to predict biodiesel densities. They have also applied a cubic-plus-association equation of state (CPA EOS) to model high-pressure density of FAMEs and biodiesels [10]. Perdomo and Gil-Villegas [11] have employed, the SAFT-VR approach [12,13] to model the vapor–liquid equilibria of three fatty acid methyl esters (FAME) biodiesel compounds and thermophysical properties of biodiesel fuel blends. Very recently, Schedemann et al. [14] have employed the volume translated Peng–Robinson (VTPR) group contribution equation of state to model their measured densities at elevated pressures for pure methyl linoleate and a rapeseed-type biodiesel. Their method led to the relative deviations within ±7%.

Physically based equations of state, derived by applying principles of statistical mechanics, have continuously been developed and improved upon over the past 4 decades. Modern equations of state aim at highly non-ideal systems, such as polymers [15], ionic liquids (ILs) [16] and associating compounds [17,18].

Yukawa hard-core chain (YHCC) model has been widely used to theoretically model a broad range of fluids in liquid state physics [19]. It has found success in modeling the thermodynamics of simple liquids, colloidal suspensions, electrolytes, and molten salts. This model involves hard-chain repulsion as well as a long-range attraction and that it describes many physical phenomena involving screened interactions. On the other hand, by varying a single parameter, λ the range of attractive forces can be easily adjusted with different interactions encountered in many physical systems [20]. With λ equal to 1.8, the model has been well-found to approximate the tail of the Lennard–Jones potential. In the perturbative scheme studied in this work, the segments are already connected. The hard-chains are chosen as the reference system, which will be perturbed by a potential.

We aim to employ the proposed perturbed hard-chain (PHC) EOS for predicting the volumetric properties of some FAMEs, methyl ester-based biodiesels and their blends. The predicted results for the density of studied systems will be compared with those estimated by the work of Pratas et al. [10].

2. Theory

2.1. Theory of perturbed Yukawa hard-core chain EOS

In perturbation theory the Helmholtz free energy (*A*) of the system is expanded in the inverse temperature around that of a reference system whose thermodynamic structural properties are known. The first-order expansion of the Helmholtz free energy is presented in Eq. (1):

$$\left(\frac{A}{Nk_BT}\right) = \left(\frac{A_0}{Nk_BT}\right) + \left(\frac{A_1}{Nk_BT}\right) \quad (1)$$

A_0 is the Helmholtz free energy of the reference system. A_1 is the first-order perturbation terms for the Helmholtz free energy. *N* is the number of molecules, k_B is the Boltzmann constant, and *T* is temperature. A_1 is derived from knowledge of the equation of state and the radial distribution function (RDF) of the reference fluid.

For the reference equation of state we employ thermodynamic perturbation theory of fluids (TPT) of Weeks–Chandler–Andersen (WCA) [21], which can be expressed by Eq. (2):

$$\frac{A_0}{Nk_BT} = \frac{A^{HS}}{Nk_BT} - (m-1)\ln g^{HC}(\sigma^+) \quad (2)$$

where, $g^{HC}(\sigma^+)$ represents the pair radial distribution function of hard-cores at contact, which was previously developed by Carnahan–Starling [22]. The first-order perturbation contribution to the Helmholtz energy can be presented by Eq. (3) [20]:

$$\frac{A_1}{Nk_BT} = \frac{-2\pi\rho m\sigma^3}{T_r} I(\eta, m, \lambda) \quad (3)$$

where, ρ is the number density of segments, *m* denotes the number of monomer sites in a chain-like molecule (chain-length) and T_r is the reduced temperature ($T_r = k_BT/\varepsilon$). η represents the segment packing fraction of hard-cores defined by:

$$\eta = \frac{m\pi\rho\sigma^3}{6} \quad (4)$$

$I(\eta,m;\lambda)$ is related to the average inter-chain function for hard-chains in the context of the Percus–Yevick (PY) integral equation theory by Chiew [23,24].

In the framework of the first order perturbation theory, the compression factor of perturbed Yukawa hard-core chain (PYHCC) may be written as [25]:

$$Z^{PYHCC} = \frac{P}{\rho k_BT} = Z^{YHCC} + Z^{Pert.} \quad (5)$$

where *P* is the pressure and k_BT is the thermal energy per segment. Z^{YHCC} represents the Yukawa hard-core chain reference system, which will be perturbed by the long-range attraction ($Z^{Pert.}$) with a